

Tutorial 3.1 – Solubility and Precipitation

Slide 1. Solubility and Precipitation

This module discusses the theory and practice of precipitation for measurable masses of materials. Radiochemistry uses several different precipitation techniques to separate and then analyze for different radionuclides. We will define several terms and introduce some new concepts used to perform these separations.

Slide 2. Learning Objectives

The learning objectives for this module are:

- Write the mathematical expression for K_{sp} given the formula of a salt.
- Calculate the concentrations of ions in solution based on the K_{sp} and concentrations of other ions present.
- Describe the phenomenon of precipitation using following terms:
 - Electrical double layer.
 - Co-precipitation.
 - Inclusion – isomorphic and non-isomorphic.
 - Occlusions.
- Explain how each type of precipitation can cause contamination of or be exploited for radiochemical separations.
- Describe the optimum conditions for producing good precipitates.

During the course of this module you will have the opportunity to self-test on these objectives. The “Key Concepts” for this module are:

- The general mathematical expression for K_{sp} is identified in the equation shown here.
- The ion that is most insoluble will be most strongly attracted to an established precipitate
- Different types of precipitate contamination that can occur.
- The purpose of coprecipitation as an analytical technique.

Slide 3. Ratios of Ionic Compounds

Ionic compounds can be separated into separate classes based on the ion ratios. On the left we have a solution that contains silver and chloride ions and the solution has excess solid silver chloride that is undissolved. The ratio of silver to chloride here is 1:1. A similar situation occurs with RaSO_4 , the ratio of radium to sulfate is also 1:1.

In the figure to the right, we have a solution that contains thorium and hydroxide ions and the solution has excess solid thorium hydroxide that is undissolved. In this case the ratio of thorium to hydroxide is 1:4. Many other combinations are possible based on the valence of the metal ion and the valence of the counter ion.

The diagram also shows some other facets relating to solubility. Notice that the precipitates are constantly dissolving, while the solution is constantly precipitating solids.

This is referred to as dynamic equilibrium, and occurs very rapidly. Also note that the number of silver ions in the saturated solution is greater than the number of thorium ions in its saturated solution. This is related to the size of the solubility constant associated with each of these salts. Thorium hydroxide has a much lower solubility than silver chloride.

For both of these solutions the liquid phase is referred to as the supernate and the solid phase as the precipitate. In both solutions the precipitate is said to be in dynamic equilibrium with the supernate and therefore the solution is “saturated.”

Slide 4. Solubility Product Constant

If we examine the equilibrium for the silver chloride example from the previous slide the expression for equilibrium is written as shown here—the solid material is on the left hand side of the equation and the ions in solution on the right hand side of the equation. Note that the subscript “s” stands for *solid* and the subscript “a” stands for *aqueous*. These subscripts are often omitted as it is usually obvious which is which. The concentration of the ions when the solution is saturated is determined empirically, that is, by experiment. Once these concentrations are known, a constant can be determined mathematically with the aid of the balanced chemical equation. The constant is called the solubility product constant and is identified as K_{sp} .

Slide 5. Solubility

Solutions containing dissolved solids can have three states: unsaturated, saturated, and supersaturated.

Picture a glass of hot tea and start adding sugar to it. The sugar dissolves readily because it is soluble in water and due to the temperature of the tea. You can repeat adding a spoon of sugar and it will dissolve as well. Eventually you reach a point where the sugar no longer dissolves but sinks to the bottom. After the addition of the first spoonful, the solution is unsaturated. That is more sugar can still dissolve. When you get to the point where the sugar drops to the bottom, you have a saturated solution.

Re-picture this instead of using hot tea using un-sweet iced tea of the same volume. What happens when you add a spoonful of sugar? You can see the sugar crystals drop to the bottom of the glass. Additionally it seems that no matter how much you stir the solution, you still have solid sugar at the bottom of the glass. In this case a saturated solution has been achieved with much less sugar because for most solids solubility decreases as a function of temperature.

A super-saturated solution is a transient state. The concentration of dissolved ions exceeds the theoretical limit. This can occur if a solution at saturation is slowly cooled. Any disturbance to the solution such as sound waves, dust particles, or stirring will cause the saturation equilibrium to instantaneously occur.

Slide 6. Mathematical Representation of the Solubility Constant

The balanced chemical equation that describes solubility of materials was shown on Slide 4. The solid, insoluble salt is written on the left hand side of the equation with a subscript of (s), indicating it is an undissolved solid. On the right hand side of the equation are the individual salt ions with the subscript (aq) indicating that they are solvated (that is, dissolved). This is the solubility product *chemical* equation for silver chloride. The amount of silver chloride that dissolves is an empirical value, and is quantified in a value called the solubility product constant or K_{sp} .

The mathematical expression that defines any kind of true chemical equilibrium is defined as the equilibrium constant and it is the multiplicative values of the product concentrations divided by the multiplicative values of the reactant concentrations. For the silver chloride solubility expression we get the mathematical expression shown here. The square parentheses around an ion symbol denote a solution concentration in units of moles per liter. Since there are no discrete molecules of silver chloride solid that are dissolved, and the solution is saturated with silver chloride, its concentration is equal to unity. The empirically determined K_{sp} value for silver chloride is 1×10^{-10} .

In general for salts with the same ion ratio the smaller the value of K_{sp} the less soluble is the salt.

Slide 7. General Equation for Solubility Constants

The general expression for K_{sp} for any saturated solution is given by the equation shown here. Note that the coefficients of the ions in the balanced chemical equation become the exponents for these same ions in the K_{sp} mathematical equation.

Now you give it a try! What is the mathematical expression for the K_{sp} for $\text{Th}(\text{OH})_4$? Click on the answer box when you have finished checking your answer.

Slide 8. Test Yourself Exercise 1

OK. Let's try a calculation. Using the equation guidance from the previous slides calculate the concentrations of barium and sulfate in a solution saturated with barium sulfate salt. Click on the hint if you need some help getting started. When you have completed your attempt go to the next slide to check your results.

Slide 9. Test yourself Exercise 1 Solution

Well how did you do? Remember that if we start with just the salt barium sulfate and equilibrate it with water, for each molecule of barium sulfate that dissolves we get one ion each of barium and sulfate.

Slide 10. Solubility Product Constant (K_{sp}) vs. Ion Product (Q)

Instead of saturating a solution with barium sulfate, what would happen if we started out with a solution of *soluble* barium nitrate and slowly added sulfate ions? Before we add any sulfate there is no precipitate. How much sulfate must we add before we get precipitation? In order to determine this we must calculate the ion product of the component ions for the insoluble salt. The ion product, denoted by the symbol –capital Q–

is calculated using the same expression that appears in the K_{sp} equation. If the concentrations for the ions are substituted in this expression and multiplied, a precipitate will occur when the value is greater than the value of K_{sp} .

Once the ion product exceeds K_{sp} we have a saturated solution of the salt.

Slide 11. Shifting the Equilibrium Towards Precipitation

So let's start out again with our solution of barium nitrate and begin adding sulfate. When the ion product exactly equals the value of K_{sp} precipitation will start. However, what happens if we keep adding sulfate? The concentration of barium ions must change to maintain the equilibrium in solution. Since the value for K_{sp} is constant the barium concentration must decrease in order to maintain equilibrium. Compare the relative number of barium ions in solution on the picture on the right to that on the left...

Slide 12. The Common Ion Effect

The phenomenon described in the previous slide is referred to as the "common ion effect." Thus, we can minimize the amount of barium ion in solution by adding more sulfate.

When performing radiochemical separations it is necessary to minimize the amount of analyte in the solution. Thus we use the common ion effect to force all the analyte into a precipitate, minimizing the amount left in solution.

Slide 13. Test Yourself Exercise 2

In this case we have made a solution 0.05 M in sulfate ion concentration. Using the principles just described can you calculate the concentration of barium in this solution when it is saturated with barium sulfate? Check your answer with the one on the next slide.

Slide 14. Test Yourself: Exercise 2 Solution

Wow! The concentration of barium is decreased by about four orders of magnitude. This common ion effect is a technique that is used to ensure minimum solubility of the radionuclides in solution.

Slide 15. Methods for Precipitating Radionuclides

There are several different techniques that are used for precipitation. One such technique, flocculation or "crash" precipitation, overwhelms a solution with precipitating agent so that a lot of ionic material is dragged out of solution with the precipitate. This has some uses in radiochemistry. Other times the radiochemist will need to use precipitation techniques that carefully control the rate of precipitate formation to eliminate other ions.

In the section that follows, we will discuss the following types of precipitation:

- Direct precipitation in the presence of a stable isotope of the same element.
- Adsorption of a radionuclide on a similar chemical precipitate via the electrical double layer effect.

- Coprecipitation as an isomorphic or non-isomorphic inclusion in a crystal.
- Coprecipitation as an occlusion or “trapped” radionuclide.

Slide 16. Direct Precipitation

There are some radionuclides that we must determine that also have stable elemental counterparts. Strontium 90 is one such radionuclide. Strontium carbonate can be directly precipitated from solution by adding excess sodium carbonate. The strontium carbonate K_{sp} is 5.4×10^{-10} , and therefore is very insoluble. But if only ^{90}Sr was present, there would be insufficient Sr concentration to exceed the K_{sp} value. So if add stable strontium, we can easily exceed the K_{sp} and not interfere with the radiochemical determination of ^{90}Sr . The stable strontium added is referred to as a carrier because it “carries” the radionuclide through the precipitation steps even though the radionuclide itself would not precipitate.

Slide 17. Adsorption to the Surface of a Precipitate

An ionic precipitate has both positive and negative charge centers on its surface. Each of these charges can attract a counter ion from solution to form the first of two ionic layers. The hydrated ion in solution, together with the counter ion on the precipitate, forms a micro-cell of concentration. The solution counter ion that will be most strongly attracted to and retained by the precipitate surface will be the ion that forms the *most insoluble compound* in that micro-cell. This “Key Concept” is the basis for precipitation of many of the actinide elements during radiochemical analysis.

Slide 18. Surface Adsorption and the Electrical Double Layer

Let’s use barium sulfate as an example, with an excess of sodium sulfate as the precipitating agent. Either sodium or sulfate can be adsorbed in the primary layer. Which of these two counter ions will form a more insoluble precipitate on the original precipitate surface? It will overwhelmingly be the sulfate since barium sulfate is insoluble and sodium sulfate is not. This can be clearly seen in the figure to the right where the sulfate forms the primary electrical layer.

Slide 19. The Electrical Double Layer

Once the most insoluble material is attracted to the surface in the first ionic layer, a counter ion must also be adsorbed to maintain electrical neutrality of the precipitate. The first layer is called the primary electrical layer and the second the secondary electrical layer. The second layer is shown in blue in the figure to the right. Together the two layers are referred to as the “electrical double layer.”

Slide 20. Significance of the Electrical Double Layer

Precipitates in solution are surrounded by an electrical double layer of solvated ions. Each layer is comprised of one type of ion either cation or anion.

The double layer has an important purpose in that it allows for the dynamic equilibrium with the supernate to occur, and it can allow for selective adsorption of certain radionuclides.

However, these ions may need to be removed for some analyses as they literally add weight to the precipitated matter. Thus washing of the precipitate with an isotonic wash is an important step in some analyses.

Slide 21. Test Yourself Exercise 3

A solution is saturated with lanthanum fluoride by tanking 1 mg of lanthanum nitrate and adding excess fluoride ion as sodium fluoride. Which of the two pictures on the right depicts the correct configuration of the electrical double layer?

Slide 22. Test Yourself Exercise 3 Solution

You should have picked B since the excess fluoride will be more insoluble at the precipitate surface than would be the excess sodium ion.

Slide 23. Characteristics of a Good Precipitate

In order to get good separations of radionuclides from other ions and other radionuclides the final form of the precipitate that is used for counting must have some important characteristics:

- Favorable stoichiometric ratio. Usually this is a 1:1 or a 1:2 salt. This is so that small quantities of common ion are needed to complete the precipitation
- Small value for K_{sp} . The smaller the value of K_{sp} the lower the solubility. This means that you get less “loss” of material into the supernatant solution.
- High mole-to-mass ratio. The equivalent number of moles needed for precipitation requires only a small mass of material. The smaller the mass of the precipitate, the less self-shielding will take place when the final precipitate is counted.
- Slow-grown, larger crystals generally desirable. This is true for those instances where a carrier material is used. This allows the material to easily remove impurities as the precipitate grows. When using coprecipitation for a final counting form, smaller crystals are more desirable.
- Not flocculent or gel-like (there are some exceptions). Flocculent precipitates trap all ions from a solution. Thus this characteristic is undesirable because good separation from contaminants would not be achieved.
- Non-hygroscopic. A material that is hygroscopic quickly adsorbs moisture from the atmosphere. The adsorbed moisture would interfere with accurate mass determination (carrier) and would attenuate the radioactive emissions prior to reaching the detector.
- Easily and quickly dried. Low temperatures and short drying times are favorable. We want to count the sample as soon as possible without special devices for drying that may lead to additional loss of our radionuclide.
- Stable mass for weighing. If the final sample test source is to be weighed to determine chemical yield, it must be stable for mass determination. Additionally, if the precipitate decomposed during the counting process it would affect the reliability of the counting source.

Slide 24. Steps in Precipitate Formation

Precipitate formation occurs in separate phases. As the ion product value approaches K_{sp} , nothing is occurring because the solution is unsaturated.

The induction period is critical especially when the precipitate is to be used as a final counting form. During this phase the ions are at the K_{sp} limit and are getting ready to precipitate.

The first nucleation site is where the K_{sp} is exceeded – this usually occurs at the point where the precipitating reagent drops touch the analyte solution. At this time if the bulk concentration of the ions in solution were used to calculate the ion product, it would likely be less than K_{sp} . However, the localized concentration of the ions is greater than K_{sp} . This approach to K_{sp} can be slowed by vigorous stirring of the solution during the addition of precipitating agent.

Once nucleation has started, the crystal growth period begins. There is short period of time when there is local supersaturation near the crystal surface.

The slow precipitation process will generally start out as colloidal material that will grow in size. The size of the precipitate and speed at which it grows is based on the relative supersaturation of the solution. Relative supersaturation can be described as the ratio of the ion product at the highest concentration point in the solution (exceeding K_{sp}) to the value of K_{sp} . The relative supersaturation is ended when the bulk solution ion product exceeds the value of K_{sp} . Small relative supersaturation leads to selective precipitation of the analyte material and avoids “crash precipitation.”

Slide 25. Precipitate Purity.

Precipitate purity is most critical at the final step in the separation process when the radionuclide in the precipitate will be counted. The radiochemists job is to ensure that the solution conditions have been adjusted to ensure the correct type of precipitate forms.

The “Key Concept” for the type of precipitate is that we have three different types that are used in radiochemistry for counting of the radionuclides. These types are:

- Isomorphic Inclusion,
- Non-Isomorphic Inclusion, and
- Occlusion.

In the next slides each of these will be discussed.

Slide 26. Isomorphic Inclusion

This type of precipitate occurs when the radionuclide under investigation is the same charge and a similar size to the precipitating agent. An isomorphic inclusion may be a mixed crystal if the radionuclide and the precipitating agent are not chemically identical. The picture on the right shows how the radionuclide, indicated by the orange sphere, takes the place of a non-radionuclide agent, indicated by the green spheres. Note that the

geometry and symmetry of the crystal structure would be the same if the orange sphere were replaced by a green sphere.

Slide 27. Examples of Isomorphic Inclusion

Isomorphic inclusion occurs in the precipitation of radium with barium sulfate. The radium is chemically similar to barium, has the same ionic charge, but is slightly larger. This would lead to a slight distortion in the crystal structure but otherwise would “fit in.” In this case the K_{sp} of radium is not exceeded, and the radium co-precipitates as a result of the isomorphic inclusion.

An example of a “perfect” isomorphic inclusion would be the use of non-radioactive strontium to precipitate ^{90}Sr as a carbonate. In this case the strontium is exactly the same size and charge and chemically the same. The stable strontium acts as a carrier to overcome the K_{sp} and the ^{90}Sr does precipitate.

Slide 28. Non-Isomorphic Inclusion

This type of precipitation occurs when two or more crystalline materials precipitate together. The precipitating agent will carry the radionuclide crystalline form out of the solution due to relatively high supersaturation and trap the radionuclide in its structure. When the actinides are co-precipitated as fluorides with lanthanum or neodymium, this is the type of precipitate that forms. The actinides will be in the +4 oxidation state and the lanthanides in the +3 oxidation state, and their crystalline structures are not exactly the same. In the figure on the right note the orange colored atom at the center of the crystal lattice shown. Although it is within the lattice it is not isomorphic with, that is the same shape as, the surrounding lattice. More on this at Slide 37.

Slide 29. Occlusion

Occlusion occurs by material being trapped randomly in a precipitate structure. This can occur during any kind of precipitation process. The occluded material may be ionic, neutral molecule, dust, or other debris. The crystal structure of the precipitating agent is significantly disturbed by occlusion. An occluded material can be removed by slowly heating the precipitate with the supernatant solution increasing the rate of dynamic equilibrium that was discussed early on in this module.

Slide 30. Example of Occlusion

Using a precipitate that will intentionally occlude a radionuclide is generally used at the early part of the separation process. A specific example is the separation of thorium from uranium using an air saturated, ammoniacal solution of iron +3. The thorium becomes occluded in the ferric hydroxide precipitate, but the uranium remains in the supernatant solution as a carbonate complex. The thorium K_{sp} is not exceeded but it co-precipitates with the ferric hydroxide.

Slide 31. Removing Contaminants from a Precipitate.

Anytime a precipitate is formed, there will be materials that contaminate the precipitate. There are different techniques that are used to purify the precipitate of these unwanted materials. One of the most common and rapid ways to purify the precipitate is by using

an isotonic wash. The isotonic wash will have the same pH and reagent concentration as the precipitating solution. This prevents a phenomenon known as peptization. Generally the isotonic wash is not the last precipitate wash, because we want to remove any ions or molecules that are part of the electrical double layer. The final cleansing wash for a precipitate is usually something that will volatilize during the filtration process. Examples of these final rinses would be solutions of hydrochloric or hydrofluoric acid, and ethanol or methanol in water.

Slide 32. Strategies for Good precipitate Formation –Part 1

Several strategies exist for formation of a good precipitate. Each strategy depends on the specific characteristic of the precipitate to be formed. For most precipitates, having an elevated temperature during the addition of precipitating agent will slow the induction and nucleation process because solubility generally increases with temperature. The precipitate can be digested to improve its crystalline structure and remove impurities. Digestion can be done by heating the precipitate with its supernatant after it is formed or by allowing the precipitate to equilibrate at room temperature with its supernatant over the course of several hours to a day.

Addition of complexing agents or common ions to increase solubility will aid in a better crystal formation. An example of this might be to load a solution of ferric ions with chloride before precipitating the hydroxide. The chloride will complex with the iron causing a slower precipitation of the hydroxide.

Another technique is to add a complexing agent that will not affect the precipitate but will affect the solubility of a specific contaminant. This was mentioned earlier in the case of uranium separation from thorium in the iron hydroxide solution. Air saturated ammonia solution is also saturated with carbon dioxide. The carbon dioxide becomes carbonate in basic ammoniacal solutions and strongly complexes with uranium, preventing its precipitation. However the carbonate does not complex with the thorium.

Slide 33. Strategies for Good Precipitate Formation- Slide 2

Remember that to form better crystalline materials we want to exclude impurities. When reagents are mixed rapidly and at high concentrations a high level of localized supersaturation is realized. This will yield a floc that will trap soluble materials within it. To help minimize this crash precipitation effect, use dilute solutions of the precipitating agent, add it slowly with vigorous stirring and gently heat the solution.

Slide 34. Carriers and Co-Precipitation

The concentration of radionuclides in drinking water samples is so low that the mass of the radionuclide is always insufficient to exceed any K_{sp} for that element. In an earlier module we had calculated that these concentrations were in the pico-molar concentration range. In order to effectively isolate these small quantities of radionuclides from the bulk sample, a non-radioactive material known as a carrier or a co-precipitating agent is added. The co-precipitant or carrier has similar properties to the radionuclide and it can be precipitated because we control its concentration.

Slide 35. Co-Precipitation of Radium with Barium

Analysis of a drinking water sample for radium requires that we use about 1 liter of sample. In order to isolate and remove the radium from the solution a pre-concentration mechanism is needed. The radium mass concentration is so small that its K_{sp} can never be exceeded. Barium and radium are both Group II elements in the periodic table. They have the same ionic charge in solution and chemically have very similar properties. This co-precipitation is an example of isomorphic inclusion.

Slide 36. Co-Precipitation of ^{90}Sr with Stable Strontium

In the analysis of ^{90}Sr stable strontium is added as a carrier to the solution. Since stable strontium has no naturally occurring radioisotopes, the mass added is sufficient to allow quantitative precipitation of the strontium that will include the chemically identical ^{90}Sr . This is also an example of isomorphic inclusion.

Slide 37. Coprecipitation of Uranium by Lanthanum Fluoride

In the case of performing uranium analysis using a lanthanum fluoride precipitate, the K_{sp} of the lanthanum is exceeded but not that of the uranium. However it is critical that the uranium be in the proper oxidation state. Only uranium in the +4 oxidation state will coprecipitate with lanthanum fluoride. The reasoning behind this will be explained in the module on REDOX.

Slide 38. Self-Absorption and Precipitate Formation

The physical mass and thickness of a precipitate used to determine a radionuclide is important. The alpha and beta particles emitted by radionuclides can only be detected if they reach the detector. If they interact with the sample precipitate before reaching the detector there will be either less or no signal recorded. This phenomenon of interaction with the sample precipitate is known as “self-absorption.” This is particularly critical in alpha analysis as alpha particles can be completely stopped by very thin slices of matter. Thus when we prepare a lanthanum fluoride precipitate for uranium analysis the final precipitate mass is on the order of 0.1 mg. This is not enough to see or weigh, but it can be reproducibly filtered—if the chemist uses the correct technique.

Slide 39. Conclusion

The principles just discussed are applied to several different radionuclide specific analyses for drinking water. You should now be able to:

- Write an expression for K_{sp} based on the balanced chemical equation for a specific reaction.
- Calculate the concentration of an ion using the mathematical expression for K_{sp} .
- Describe how to prepare good quality precipitates for radiochemical analysis.
- Describe how and why stable carriers are used in radiochemical separations.